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**by Thomas F. Juliano, Aaron M. Forster, Peter L. Drzal, Tusit Weerasooriya,  
Paul Moy, and Mark R. VanLandingham**

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# Multiscale mechanical characterization of biomimetic physically associating gels

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The mechanical response of living tissue is important to understanding the injury-risk associated with impact events. Often, ballistic gelatin or synthetic materials are developed to serve as tissue surrogates in mechanical testing. Unfortunately, current materials are not optimal and present several experimental challenges. Bulk measurement techniques, such as compression and shear testing geometries, do not fully represent the stress states and rate of loading experienced in an actual impact event. Indentation testing induces deviatoric stress states as well as strain rates not typically available to bulk measurement equipment. In this work, a ballistic gelatin and two styrene-isoprene triblock copolymer gels are tested and compared using both macroscale and microscale measurements. A methodology is presented to conduct instrumented indentation experiments on materials with a modulus far below 1 MPa. The synthetic triblock copolymer gels were much easier to test than the ballistic gelatin. Compared to ballistic gelatin, both copolymer gels were found to have a greater degree of thermal stability. All of the materials exhibit strain-rate dependence, although the magnitude of dependence was a function of the loading rate and testing method.

## I. INTRODUCTION

Blunt trauma may have significant detrimental effects on thoracic organs, and understanding these effects is critical for the design of protective equipment used in automotive, body armor, and sports applications, among others. Improved understanding of energy dissipation and damage assessment is needed to model interactions between human soft tissue, personnel protective equipment, and the impact source. Experiments using cadavers, instrumented dummies, and synthetic biomimetic materials measure and model effects of extreme pressure and velocity on soft tissue. As a result, standard tests and surrogate materials have been developed to evaluate and rank protective equipment.<sup>1</sup>

Recent work to better understand how impact forces are transmitted through soft tissue have led to the fabrication of instrumented surrogate torsos composed of modified ballistic gelatin (BG)<sup>2</sup> or modified silicones.<sup>3</sup> To an extent, these testing platforms mimic the mechanical response of soft tissue and are often instrumented to gather pressure and velocity data during impact. This data is further utilized to validate finite element models, which help to describe the response of the soft tissue. Often lacking in these efforts is the proper match of the surrogate mechanical properties to soft tissue mechanical properties. A closer pairing of the acoustic and mechanical properties of a well-defined synthetic material to natural tissue can improve the data collected from the surrogates, ultimately improving the ability to model impact damage.

Naturally derived BG has been most widely used as a tissue surrogate to develop a wound profile that provides limited injury analysis.<sup>4,5</sup> For over 40 years, BG has been a standard test medium for evaluating the effects of ballistics and firearms on soft tissue.<sup>6,7</sup> BG is a

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thermoreversible material formed from polypeptide chains dissolved in water. It is crosslinked by collagen-like strands that aggregate to form a triple helix structure. Previous research has shown that the elastic modulus of soft tissue varies from 25 to 300 kPa<sup>8</sup> with the modulus of BG being approximately 100–150 kPa.<sup>9,10</sup> It is readily available, cheap, and easy to process. However, challenges in using BG as a standard test medium are significant. The mechanical properties, for example, are related to the concentration of water in the gelatin, and so water evaporation dramatically alters the mechanical properties. Ideally, model gels would be tested at 37 °C, normal body temperature, but gelatin provides usable tissue mimetic properties only within a narrow temperature range of 3–30 °C. Naturally derived gelatin is polydisperse and can have a variable molecular-weight distribution that can lead to inconsistent gelatin properties from batch to batch. Finally, while a properly formed natural gelatin is a homogenous material, procedural differences exist with regard to gelatin processing and testing.<sup>2,7–10</sup> These procedural differences lead to gelatins of differing mechanical properties and make comparisons between manufacturers, testing labs, and researchers difficult.

Any surrogate material selected to mitigate these issues and replace BG should possess a well-defined molecular weight or crosslink density to ensure identical gels from batch to batch. The material should exhibit stable mechanical properties as a function of time and temperature relevant to testing conditions. The material should also mimic natural tissue mechanical properties as closely as possible. Ultimately, this is a challenge because biological tissue is a non-isotropic material. Triblock copolymers possessing an *A-B-A* polymer structure, dissolved in a solvent selective for block *B*, are potential candidates as surrogate materials. The elastic modulus of these gels is primarily determined by the molecular weight of the *B* block (molecular weight between entanglements) and the polymer concentration. By adjusting the concentration of polymer in the gel or the molecular weight of the *B* blocks, the elastic modulus of the gels can be tailored to mimic the elastic modulus of different types of soft tissue.

The time and strain dependent mechanical properties of these gels are determined by the temperature-dependent solubility of the *A* block in the selective solvent. At elevated temperatures, where both the *A* and *B* chains are dissolved, a freely flowing solution exists. As the temperature is lowered through the order-disorder temperature,  $T_{ODT}$ , the *A* block chains precipitate and aggregate giving rise to the network structure responsible for the gel elasticity. In this state, however, the *A* block aggregates are still swollen with solvent. The network structure is viscoelastic because the *A* block chains can exchange between aggregates to minimize an applied

stress.<sup>11,12</sup> As the temperature is lowered further from the  $T_{ODT}$ , the energy required to pull chains from the *A* aggregates increases as the *A* domains become less soluble and less swollen. If the temperature is further lowered below the glass transition temperature of the *A* blocks, the gel becomes highly elastic and exhibits long relaxation times characteristic of the glassy nature of the aggregates. The mechanical properties of a variety of *ABA* type gels have been extensively evaluated in the literature.<sup>13–18</sup> A triblock copolymer gel serves as an excellent starting point for a surrogate material because these gels exhibit predictable mechanical behavior over a known temperature range, the mechanical properties are relatively stable over time, and the gel mechanical properties may be tuned by changing solvent selectivity, triblock copolymer composition, and temperature.

Techniques such as quasi-static and dynamic compression and torsion tests can be used to evaluate the mechanical properties of gels on the macro-scale, and instrumented indentation<sup>19</sup> can be utilized to measure the mechanical properties of these materials at the micro-scale. The size scale of the indenter is adequate for investigating heterogeneity on the order of microns.<sup>20,21</sup> Instrumented indentation has been used to characterize quasi-static and dynamic properties of thermoset polymers and elastomers.<sup>22,23</sup> There have been numerous efforts to model the viscoelastic response of polymers to indentation based on the use of Kelvin and Voigt elements to develop constitutive relations.<sup>24–27</sup> In the case of polymeric materials, the tip-sample interaction is of critical importance<sup>28</sup> because polymers exhibit strain rate sensitivity and time-dependent mechanical phenomena such as creep and stress relaxation.

The use of instrumented indentation for evaluating tissue surrogates is advantageous because the surface compression loading is similar to that of a blunt impact into soft tissue. Also, current instrumented indentation testing machines permit the exploration of strain rates, stress states, and resolution of measurement not achievable utilizing conventional mechanical tests, although the current methodologies for modeling tip-sample interactions are limited.<sup>29,30</sup> The theoretical capabilities of these indentation systems include the resolution of displacements below 1 nm and forces below 1  $\mu$ N, with measurements on materials possessing an elastic modulus above 1 MPa readily achieved. Significant challenges exist when conducting measurements on materials with an elastic modulus below 1 MPa using contact diameters of just a few  $\mu$ m. Adhesion between the indenter tip and sample surface affect the governing displacement-based Hertzian contact area approximation used to determine the contact area that in turn affects the mechanical property calculations.

In this work, the mechanical behavior of a traditional BG is compared to two different physically associating

gels. A methodology is described to conduct surface mechanical property measurements, using instrumented indentation, on soft gel systems ( $E < 1$  MPa). Second, a comparison is made using both bulk and surface measurement techniques to highlight the similarities and differences between the materials at differing length scales and frequency regimes.

## II. THEORY

The governing equations for determining the modulus of elasticity from compression and torsion tests are readily available in the literature.<sup>31</sup> Thus, the discussion that proceeds is focused on the contact mechanics required to measure the mechanical properties of gels through instrumented indentation utilizing a cylindrical flat punch in an axisymmetric geometry. The cylindrical punch was chosen because the uncertainty in the contact area is not significant compared to other tip geometries, leading to smaller error in measured mechanical properties.

When analyzing bulk compression test data, load and displacement measurements must be converted into stress and strain to obtain the modulus of elasticity. For a cylindrical specimen, the average engineering stress is computed as the load divided by the cross-sectional contact area and the engineering strain as the ratio of change in specimen length to original length. The modulus values reported in this work are the ratio of the average engineering stress to engineering strain in the elastic regime.

To convert indentation loading data into a modulus value, a relation from contact mechanics<sup>20</sup> is used:

$$E^* = \frac{P}{2rh} \quad , \quad (1)$$

where  $E^*$  is the reduced modulus of the indented material,  $r$  is the cylindrical radius of the indenter, and  $h$  is the displacement into the surface. The reduced modulus is defined as

$$E^* = \left[ \frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \right]^{-1} \quad , \quad (2)$$

where  $\nu$  and  $E$  are the Poisson's ratio and elastic modulus of the indented material, respectively, and the subscript  $i$  refers to properties of the indenter. If the indenter tip is taken to be perfectly rigid, and the material is assumed to be purely elastic, isotropic and incompressible, the indented material modulus becomes

$$E = \frac{3P}{8rh} \quad . \quad (3)$$

For time-dependent materials, the modulus measurement is represented by a complex modulus, or the vector

sum of the storage and loss modulus. Note that this equation is valid only for a cylindrical flat punch. Relationships for other geometries, i.e., spherical or conical tips, will have different relationships between modulus, load, and displacement, and will also include a continuously changing contact area, which is often difficult to accurately predict for very soft materials without optically measuring contact area.

Traditionally, storage and loss moduli are calculated by considering the phase difference  $\delta$  between an applied oscillating shear stress or strain, and the delay in material response as a function of time. In shear, the storage and loss modulus are

$$G' = G \cos \delta \quad , \quad (4)$$

and

$$G'' = G \sin \delta \quad , \quad (5)$$

respectively, where  $G$  is the ratio of the applied shear stress amplitude to shear strain amplitude. To equate these with uniaxial storage and loss moduli values for an incompressible elastic solid, the relation

$$E = 3G \quad , \quad (6)$$

is used.

For indentation with a flat punch, storage and loss moduli are calculated in the following way. Assuming isotropic, elastic and incompressible contact, storage modulus is a function of the dynamically measured stiffness  $S$  (or an instantaneous ratio of load to displacement) and is given by

$$E' = \frac{3S}{8r} \quad . \quad (7)$$

This is essentially identical to Eq. (3), except that stiffness is measured dynamically instead of from the loading or unloading curve. The loss modulus is a function of the measured damping,  $C$ , associated with the contact, along with the excitation frequency  $\omega$  and is given by

$$E'' = \frac{3\omega C}{8r} \quad . \quad (8)$$

These relations have been shown to be valid for different polymeric systems.<sup>23,32,33</sup>

Mechanical properties provide an evaluation of the structural integrity of a material as a function of experimental variables. For a blunt trauma test, it is desirable to develop a measure of a material's ability to dissipate impact energy as a function of both force and displacement rate. The energy per unit volume may be used to describe the energy expended to deform the surface and sub-surface material. Energy per unit volume is calculated from a compression test using the total area underneath the stress-strain curve up to a given strain value.



This area will have standard units of  $\text{J/m}^3$  and represents the total amount of mechanical energy absorbed by a normalized volume of material. When considering indentation with a flat punch, the area underneath the load-displacement curve is the energy only, with units of  $\text{N} \cdot \text{m}$  or  $\text{J}$ . To normalize this amount by a unit volume, the total displaced volume is determined by

$$V = \pi r^2 h \quad (9)$$

The relations in this section are used extensively to compute reported values in this work.

### III. EXPERIMENTAL

Ballistic gelatin (BG) samples were made from a 20% mass fraction of 250 bloom type A ordnance gelatin dissolved into 40 °C ultrapure filtered water. The aqueous solution was centrifuged for 15 s to remove solids. Right cylinder compression specimens were fabricated by pouring the solution into an open-faced aluminum mold and cooling to ambient conditions. The diameter and length of the specimen geometry are 50.8 mm and 12.7 mm, respectively, thus yielding a length to diameter ratio of 4.

Physically associating gels were made from two triblock copolymers (Kraton Polymers, Houston, TX) consisting of polystyrene (PS) and polyisoprene (PI). Both triblock copolymers consisted of 80% mass fraction triblock (PS-PI-PS) and 20% mass fraction diblock (PS-PI) composition. One gel contained 15% by mass PS (PS-15), and the other gel contained 30% by mass PS (PS-30), both used as received. The polymer was mixed with white, light mineral oil (Mallinckrodt Chemicals, St. Louis, MO) at a ratio of 20% by volume polymer and 80% by volume mineral oil. The solution was placed in a nitrogen-purged vacuum oven at  $\sim 150$  °C and fully dissolved over a period of about 6 h, being stirred every hour. The melt was then poured onto a flat surface where it was allowed to cool and gelate, with the PI chains bridging aggregate PS crosslinks. Both materials were visually transparent and contained no detectable bubbles in their final state.

The bulk mechanical properties of the BG, PS-15, and PS-30 were obtained using an Advanced Rheometer 2000 (TA Instruments, New Castle, DE) and a servo-hydraulic Instron 1331 mechanical testing frame (MTS Systems, Eden Prairie, MN). The rheometer has a force resolution of about 10  $\mu\text{N}$  and a displacement resolution of about 1  $\mu\text{m}$ , capable of both compression and tension testing. A 4.44 kN capacity load cell was used with the Instron machine to reduce the signal to noise ratio when testing soft materials. The force resolution of the load cell is about 0.5 mN, and displacement resolution is about 3  $\mu\text{m}$ .

BG was tested at  $10 \pm 0.1$  °C in compression using the Instron machine at controlled strain rates of 0.001 and

0.01  $\text{s}^{-1}$ . Twenty different samples comprised the data set. Compression tests for PS-15 and PS-30 were performed on the rheometer at room temperature using 12-mm-diameter cylindrical specimens that had a thickness of approximately 3 mm. Tests were displacement controlled at rates of 5, 10, 50, and 100  $\mu\text{m/s}$ , until a total of 500  $\mu\text{m}$  displacement occurred, yielding equivalent strain rates of approximately 0.0017, 0.0033, 0.0167, and 0.0333  $\text{s}^{-1}$ , respectively. In compression experiments for BG, PS-15, and PS-30, the loading surfaces of the test samples were well lubricated with mineral oil to ensure a uniaxial stress state and to reduce frictional effects. The diameter of the loading plates was larger than the specimen diameter and was polished to a mirror finish to reduce the friction between the specimen and loading platens. Reported modulus values were computed for each compression test from a least-squares fit of the experimental data. To further investigate the mechanical properties of these three materials, dynamic tests were performed on the rheometer within the temperature range of 0–50 °C in torsion using oscillation frequencies of 0.1 and 10 Hz.

PS-15 and PS-30 mechanical properties were measured at the micro-scale using a TriboScope depth-sensing indenter (Hysitron, Inc., Minneapolis, MN). Load and displacement are continuously measured during material loading and unloading at resolutions in the sub- $\mu\text{N}$  and sub-nm range, respectively. For all tests performed in this work, a 250- $\mu\text{m}$  radius flat punch indenter was used. The material surface was located by manually lowering the tip until an adhesive tensile force was sensed (a negative force). The indenter was lowered until the load reading became zero (Fig. 1). Quasistatic indentation tests to a maximum of 600 nm were carried out at 1, 10, 25, 50, 100, 150, and 200  $\mu\text{N/s}$  controlled loading rates. Unloading rates were approximately the same for each test, and holding times were less than four seconds. Data points were collected using active load control, meaning the spring force was subtracted from the measured load in real time to achieve true loading rates. Dynamic tests were performed at depths of approximately 500 nm into the sample surface with oscillation amplitudes of about 15 nm. Oscillation frequency varied from 10 to 200 Hz. Indentation data are not reported on BG due to non-repeatability of tests. It was experimentally difficult to obtain repeatable tests since the properties of BG change so drastically with temperature (see Fig. 2) and relative humidity. The mechanical and geometrical stabilities both were affected by inhomogeneity of the gelatin and evaporation of water from the surface.

### IV. RESULTS AND DISCUSSION

Bulk compression measurements at  $\sim 10$  °C indicate BG modulus values of  $96 \pm 12$  kPa at a strain rate of



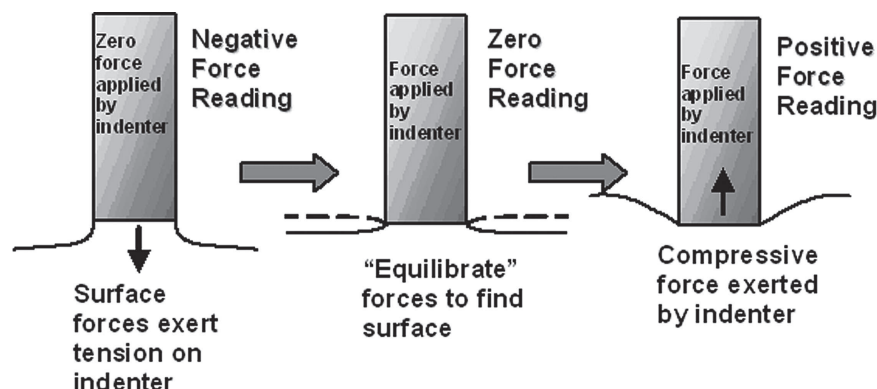


FIG. 1. Evolution of measured forces between the indenter and gel in determining the initial point of contact and during loading.

$0.001 \text{ s}^{-1}$  and  $124 \pm 4 \text{ kPa}$  at a strain rate of  $0.01 \text{ s}^{-1}$  to ultimate strains of about 1. The dependence of modulus on strain rate suggests that BG has a significant viscoelastic component to its mechanical behavior. Dynamic measurements from rheometer experiments confirm this as well. At 0.1 and 10 Hz excitation frequencies, the corresponding loss modulus values were calculated to be approximately 20% of the storage modulus at  $10^\circ\text{C}$  (Fig. 2). Storage modulus was about 150 kPa while the loss modulus was about 30 kPa. In theory, the complex modulus (or just “modulus” as it is referred to here) is the vector sum of the storage and loss modulus, which are perpendicular to each other, or about 153 kPa in this case. The modulus measured by compression should be, and is, equal to or less than this value. A major weakness of BG, as can be seen from Fig. 2, is the loss of the gelatin structure between 25 and  $30^\circ\text{C}$  over a period of time, making testing at room temperature unreliable.

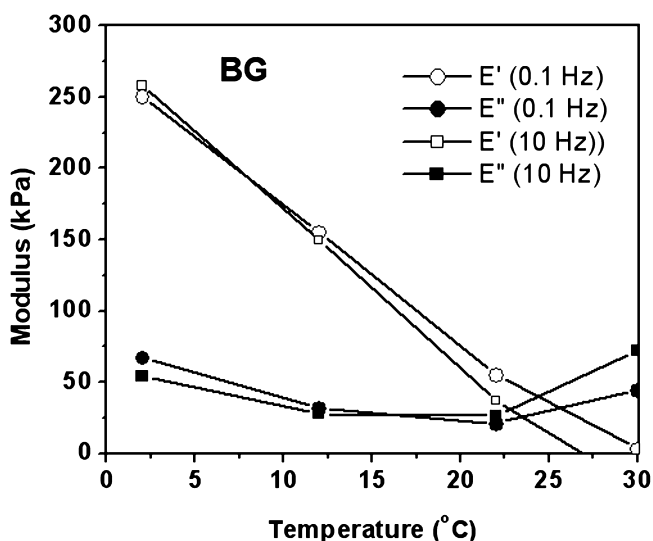


FIG. 2. Storage and loss modulus properties for BG as measured dynamically at 0.1 and 10 Hz with the rheometer from 0 to  $30^\circ\text{C}$ . Properties vary greatly as a function of temperature

Gel compression tests at room temperature for both PS-15 and PS-30 showed virtually no rate dependence in the considered loading range of 5–100  $\mu\text{m/s}$ . Figure 3 illustrates the averaged modulus data along with standard deviations for ten different runs. For all tests, the average modulus value for PS-15 is lower than that for PS-30; however, for two of the loading rate conditions, the values are within the standard deviation of the measurements. As compared to BG, the synthetic gel modulus values are significantly lower (by a factor of 4–5). Dynamic measurements, shown in Fig. 4, agree with the compression test data trends at room temperature. The complex modulus values of PS-15 and PS-30 are approximately 18 and 30 kPa, respectively. It is unclear why such a detectable modulus difference exists using the dynamic method as compared to quasistatic uniaxial compression, although the two techniques agree better for the PS gels than for the BG. This could be due to the fact that the compression samples had lubricated

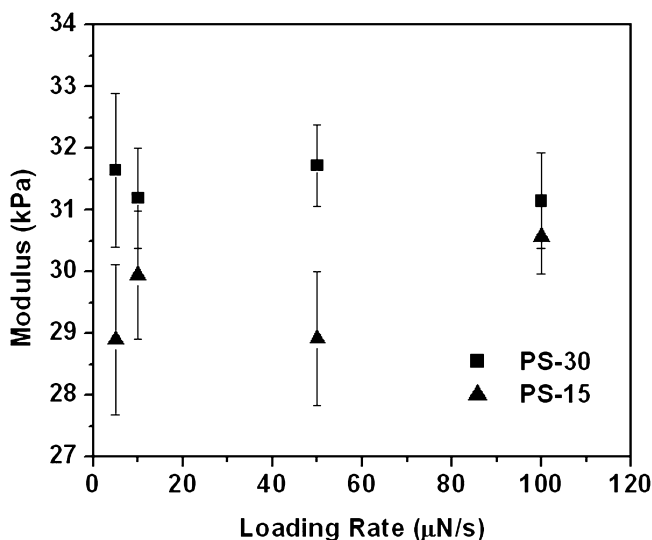
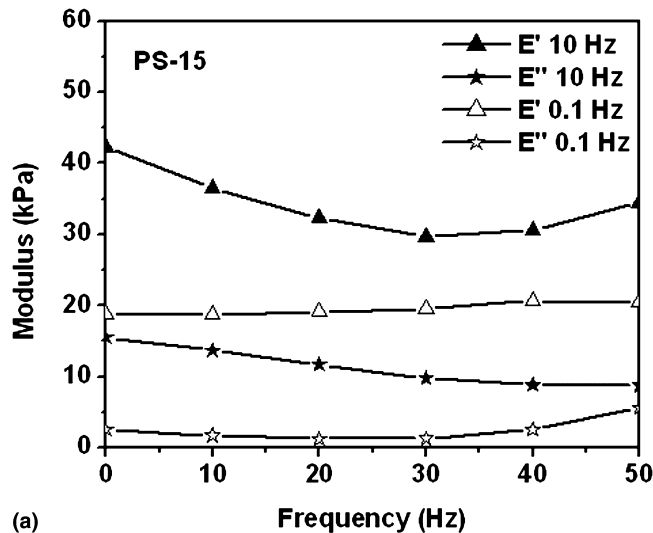
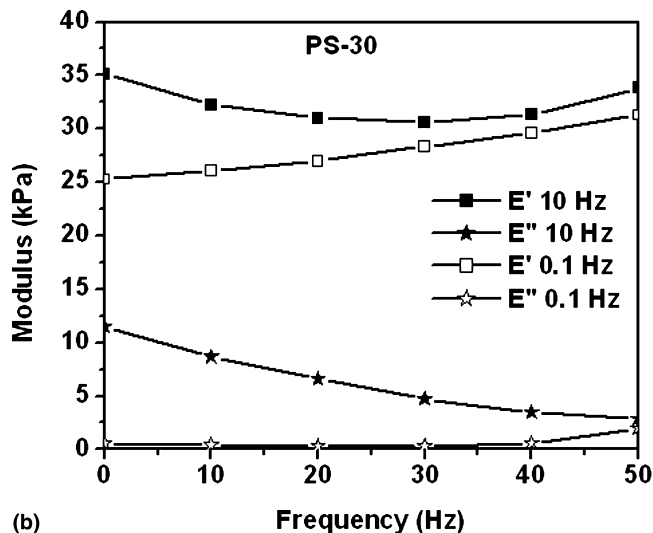


FIG. 3. Compression test data for PS-15 and PS-30 at loading rates of 5, 10, 50, and 100  $\mu\text{m/s}$ . Error bars show one standard deviation.



(a)



(b)

FIG. 4. Storage and loss modulus properties for (a) PS-15 and (b) PS-30 measured dynamically at 0.1 and 10 Hz with the rheometer in the temperature range of 0–50 °C.

boundaries while the dynamically measured samples did not. Dynamic measurement may also cause a localized heating effect in the sample, inducing a lack of thermal equilibrium in the material. Unlike BG, PS-15, and PS-30 have fairly stable mechanical properties in the range of 0–50 °C, which make their properties easier to assess at room temperature compared to BG.

Indentation measurements were conducted to compare microscale mechanical properties to those measured at the macroscale. Quasistatic indentation tests on PS-15 and PS-30 yielded a rate-dependent hardening response that was not seen with the compression tests. For both gels, a higher loading rate yielded a higher load at the same displacement into the surface. An example of this effect is seen in Fig. 5. Only the linear portions of the loading curves in Fig. 5 were considered for modulus measurements (typically from approximately 100–600 nm

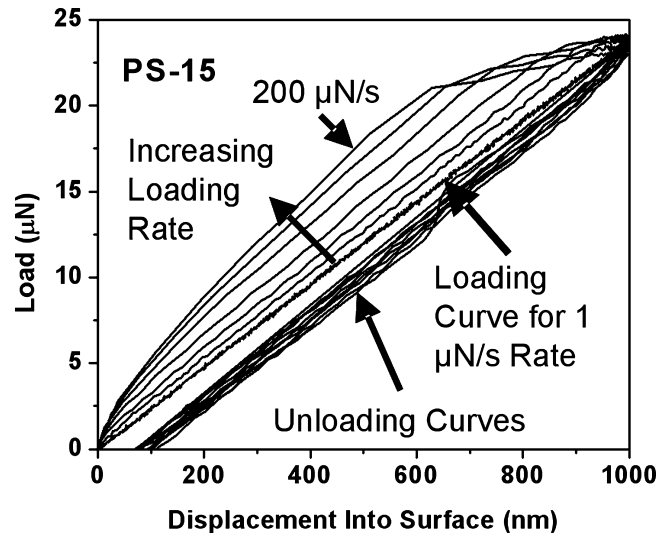


FIG. 5. Loading and unloading curves for loading rates of 1, 10, 25, 50, 100, 150, and 200  $\mu\text{N/s}$  on PS-15, illustrating the time-dependent response of the material. Results were similar for PS-30.

indentation depth). The nonlinear portions of the loading curves are believed to be due to the inertia of the indenter fixture and artifacts from the closed-loop control system and thus are discarded from the analysis. Because these measurements are based on Eq. (3), the measured modulus represents a vector sum of the storage and loss modulus. If the assumptions made are correct, the  $P$  versus  $h$  plot should be linear for a flat punch. Therefore, the slope of the line is critical to determining the measured modulus, while the origin of the fit will not influence the measured modulus. This is not the case with other indenter geometries such as spherical, Berkovich, conical, or cube corner.

Modulus values for PS-15 and PS-30 as a function of loading rate are reported in Fig. 6. Interestingly, the modulus of PS-15 is lower than that for PS-30 at loading rates below 50  $\mu\text{N/s}$ , and above this rate, the modulus values are within the standard deviation of each other ( $\sim 1$  kPa). It is possible that at such high loading rates, this behavior is an artifact of the machine's collection capabilities, or it could point to the fact that the mobility for each material becomes similar at higher loading rates. For stress rate comparison, the stress rate during indentation loading at 50  $\mu\text{N/s}$  was similar to the rheometer loading rate of 10  $\mu\text{m/s}$ . Unfortunately, this comparison is not valid for strain rate because the indentation strain rate (loading rate divided by load) continually changes with indentation depth during a constant loading rate test.

The major noticeable difference between the quasistatic compression data and the indentation data for PS-15 and PS-30 is the evidence for rate dependence in the materials. Although the average stress in the direction of applied force during indentation is much less than for compression tests, the stress field underneath the flat

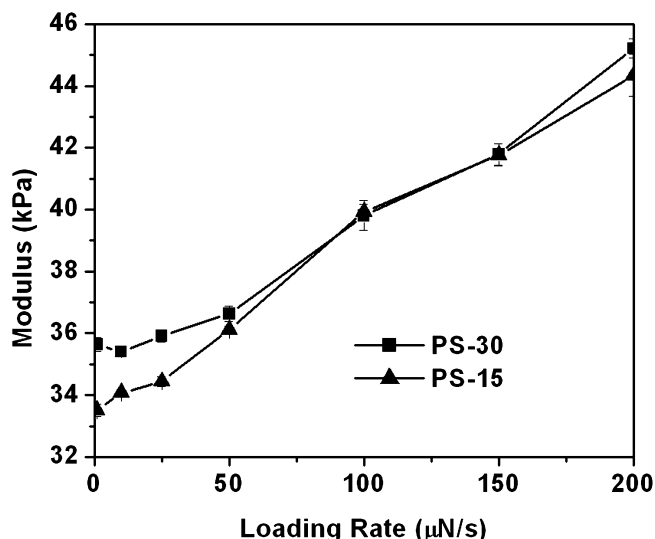


FIG. 6. Indentation modulus of PS-15 and PS-30 as a function of loading rate. Error bars represent one standard deviation in the measurements.

punch indenter is much different from that for uniaxial compression. For example, at about 85% of the radius value, the stress underneath the tool is twice the stress incurred at the center of the flat punch. Uniaxial compression assumes an evenly distributed stress state in the direction of loading. However, at the edge of the flat punch, stresses are very large (theoretically infinite). Therefore, this highly stressed annular boundary area, which is not present in bulk compression tests, may contribute to the rate dependence of the two materials.

Likewise, the modulus measured by the indentation technique is also higher than that for compression. A reason for the higher modulus may be tensile stress buildup that contributes to frictional forces, as the incompressible gel material is stretched across the face of the indenter. The average storage modulus of both PS gels was  $47 \pm 8$  kPa, and the loss modulus was  $2.4 \pm 1.0$  kPa when the data were averaged over the frequency range of 10–200 Hz, as measured by dynamic indentation. These averages yield complex modulus values only slightly higher than those found using the quasistatic indentation technique, which could be due to heating effects at higher frequencies. However, the measured storage and loss modulus varies quite a bit over the frequency range (Fig. 7). At 10 Hz, both materials had a storage modulus of 39 kPa, which is still higher than values determined using the rheometer, but are within close agreement of the quasistatic data. This discrepancy between indentation storage modulus and the rheometer values may be dependent on the calibrated dynamic response of the indentation instrument, which has a much greater stiffness than that of the contact. Therefore, the dynamic contact stiffness and damping measurements may not be sufficiently sensitive to properly sense the contact.

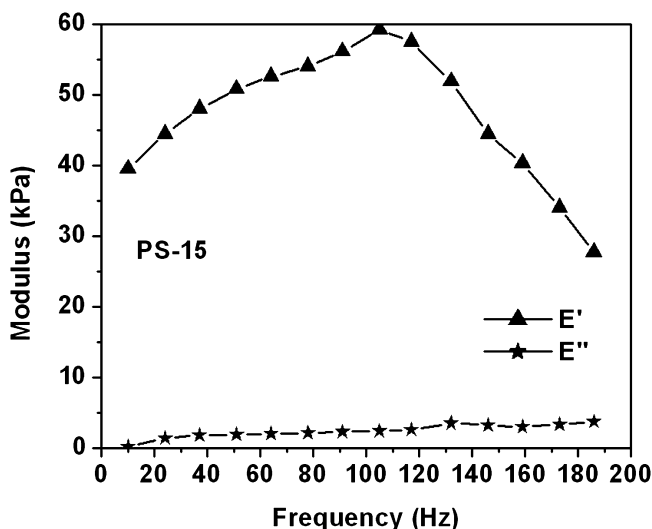


FIG. 7. Storage and loss modulus of PS-15 as measured dynamically with the flat punch indenter over a range of 10–200 Hz. Results for PS-30 were similar.

Similar to the trend with the loss modulus measured via the rheometer, there is a consistent increase in its magnitude as a function of frequency. Time–temperature superposition measurements (not shown) made via the rheometer and shifted to frequencies above 100 Hz show a monotonically increasing modulus compared to the decreasing modulus observed in this range for the dynamic indentation measurements. As measured with indentation, the loss modulus is  $0.20 \pm 0.03$  kPa at 10 Hz and  $3.7 \pm 0.1$  kPa at 200 Hz for both PS-15 and PS-30. The loss modulus was 0.5% of the storage modulus at 10 Hz and 16% at 200 Hz.

Because the materials in this study are used to examine projectile penetration characteristics, it is also useful to consider how much energy per unit volume is absorbed by each material during an impact. This will not be a perfect correlation because the magnitude of strain rates seen during a ballistic event ( $\sim 1,000$ – $10,000$  s<sup>-1</sup>) are much higher than those for indentation ( $\sim 0.01$ – $100$  s<sup>-1</sup>), but insight can still be gained. In either case, the higher the impact energy, the greater the toughness of the material required to absorb the projectile without critical failure. The absorbed energy will change depending on the displacement during the compression test, the sample thickness, or displacement into the surface for an indentation test. For BG, the energy per unit volume as a function of displacement during compression for 0.001 and 0.01 s<sup>-1</sup> strain rates is compared to test data on PS-15 and PS-30 [Fig. 8(a)]. For PS-15 and PS-30, there was no energy per unit volume dependence on strain rate. Under uniaxial loading, the energy per unit volume increase is exponential with displacement. For any loading geometry, the energy per unit volume magnitude as a function of displacement trends with the measured modulus value

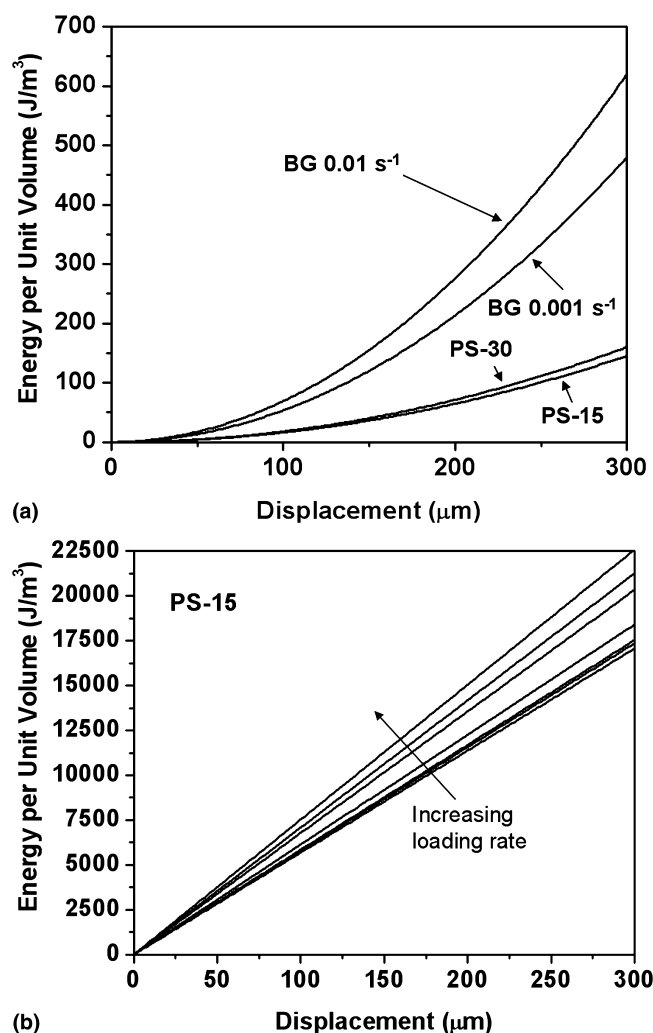


FIG. 8. Energy per unit volume as a function of displacement for (a) a compression test and (b) a flat punch indentation test. Compression test data show a comparison between energy absorbed under similar loading conditions for BG at 0.001 and  $0.01 \text{ s}^{-1}$  and PS-15 and PS-30 (extrapolated to  $300 \mu\text{m}$  penetrations). Energy absorbed by PS-15 in (b) was similar to that absorbed by PS-30, although PS-30 was slightly higher.

only. Figure 8(b) shows a comparison between PS-15 and PS-30 for the flat punch loading geometry. Because BG could not be tested at the microscale, no similar comparison was conducted. PS-30 absorbs more energy at the various loading rates than PS-15 (i.e., has a higher modulus), especially at lower loading rates. This is possibly a reflection of the higher force required to remove individual PS chains from larger crosslinks of this material.

Between the two different loading geometries used in this study (or between any two loading geometries), the energy per unit volume comparison for the same material is most useful. Approximately two hundred times more energy is absorbed in the indentation tests at  $300 \mu\text{m}$  (extrapolated) for PS-15 and PS-30 than in the compression tests. This comparison suggests the degree

to which a  $500\text{-}\mu\text{m}$  diameter flat punch penetrator may cause failure to an impacted material compared to a large blunt force. In the future, different penetrator geometries will be examined to determine the degree of impact damage from variously shaped projectiles.

## V. CONCLUSIONS

The modulus of BG was successfully measured at  $10^\circ\text{C}$  using quasistatic and dynamic techniques on the macroscale. Two physically associating gels, PS-15 and PS-30, based on swollen triblock copolymers, were found to exhibit quasistatic properties within the range of BG. Although the modulus values of PS-15 and PS-30 were less than BG, they were still at the lower end of the modulus range reported for soft tissue ( $\sim 25 \text{ kPa}$ ). Even though only two specific gels were studied in this work, the gel systems may be tailored to have their modulus increased. Compared to BG, both PS-15 and PS-30 were found to have a greater degree of thermal stability. BG gels have a shelf life of just a few days at ambient conditions. A successful methodology was developed for mechanically characterizing materials with a modulus below  $1 \text{ MPa}$  using instrumented indentation, which applies to a number of other soft material systems. Both macro- and microscale tests of PS-15 and PS-30 yielded similar modulus measurements. Macroscale measurements found little rate dependence on either PS-15 or PS-30, while microscale measurements revealed rate dependent behavior. The reason for this difference was thought to be due to the boundary conditions present during flat punch indentation as compared to a compression test. Interpretation of the dynamic mechanical properties of the two gels measured with instrumented indentation and comparisons to the loading rate effects were difficult. More extensive work on these and other similar material systems is planned for the future.

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Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the Army Research Lab nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

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